

INTERFACIAL PROPERTIES OF ACID, BASIC AND NEUTRAL FRACTIONS DERIVED FROM ORINOCO BELT CRUDE OIL,

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INTRODUCTION

The interfacial properties of acid fractions play an important role in the stabilization of crude/water emulsions mainly because of their behavior as natural surfactants [1-13]. Also, acid compounds are used as biomarkers in geochemical correlations [14]. On the other hand, acid fraction are known to be coke precursor compounds [14], contributed to deactivation of heterogeneous catalysts used in refining operations and to stabilize water/crude oil emulsions making difficult crude dehydration during oil production processes [10-14].

In 1956, Reisberg and Doscher [1] demonstrated that interfacially active components present in Ventura crude oil are of acidic nature, whereas, in 1964, Newman [2] reported that the later fraction is constituted mainly of phenolic compounds for a Eichlingen-Niedersachsen crude. From these studies and for a Rio Bravo crude oil, Bartle and Niederhausen [3] concluded that the interfacially active materials are concentrated principally in the resins and asphaltene fractions.

Schramm and coworkers [4] studied the influence of the concentration of indigenous surfactants on the recovery of Athabasca bitumen using steam at high pH values. The interfacially active components were separated from the crude oil using the tendency of the former substances to concentrate at the interface of a foam. Using this method, the authors proposed [4] a general chemical structure which consists of naphtenic rings with carboxylic acid substituents. The surfactants (R-O⁻) were generated by addition of sodium hydroxide (eq. 1) in order to enhance bitumen separation from the oil sand [4].



Unfortunately, the extraction of the natural surfactant at high pH value (>10) can generate species, via hydrolysis (eq. 2), which were not originally present in the crude oil. These new species may present substantially different interfacial activity than that found for the indigenous compounds [7-8].



Speight and coworkers [5] extracted phenolic and carboxylic acid compounds from Athabasca bitumen using solvents of different polarities and ion-exchange resins. The authors concluded that oxygenated compounds present in the asphaltene fraction have phenolic substituents, whereas resins concentrate the carboxylic acid moieties [6]. No details were given on the interfacial activity of the isolated fractions.

Seifert and Howells [7-8] extracted anionic compounds with NaOH/EtOH from a parafinic crude oil (Midway-Sunset) and characterized the interfacially active compounds at pH values greater than 10. By comparison of interfacial tension vs pH of the original crude and its acid fractions (strong and weak), the authors concluded that their extraction method was efficient for the isolation of the surface active compounds. However, the authors reported the generation, via hydrolysis (eq. 2), between 40 and 50% of tensoactive materials which was not originally present in the crude oil [7-8].

Acevedo *et al.* [9] studied the interfacial activity of SARA fractions separated from Orinoco Belt crude oils and concluded that natural surfactants were present mainly in the resin fractions. From interfacial tension vs pH determinations for the crude oil and its extracts and the lower molecular weights found for methylated asphaltenes, the author suggested that carboxylic acid species were responsible for the observed interfacial activity. However, no further characterization were reported [9].

Sjblom and coworkers [10-12] extracted surface active compounds from North Sea crude oil using a consecutive adsorption technique. The interfacial properties of the extracted fractions were evaluated using a decane/water (1:1) model system. It was found that the interfacial tension decreased and the stability of the emulsion w/o formed was higher as the polarity of the fraction increased. Sjblom *et al.* [13] found a molecular weight for the indigenous surfactants between 900 and 1500 g/mole and, based on spectroscopic methods, proposed an average structure which

contains a long alkyl chain bonded with phenol, nitrogen or carboxylic acid substituents. However, the effects of the presence of strong (carboxylic) and weak (phenols) acids on the surface activity of the indigenous surfactants were not studied in detail.

From the previous literature, it can be concluded that the relationships between chemical structure and surface activity of acid fractions, which in turn at higher pH values behave as natural surfactants, are still widely unknown. Furthermore, the effects of the nature of the hydrocarbon chain, R, on the interfacial properties of these fractions have not been addressed in detail. This R group controls not only the acid strength (pKa) of an anionic surfactant but also its hydrophilic-lipophilic balance.

In this work, acid, basic and neutral fractions from Orinoco Belt Crude Oil (Cerro Negro) were isolated by ion-exchange chromatography and characterized by spectroscopic methods (FTIR, H- and ^{13}C -NMR), titration with KOH and molecular weight measurements using vapor pressure osmometry (VPO). The ion-exchange chromatography method was chosen because it is based on separation by functional group, induces little changes on the nature of the crude oils and reasonable mass balances can be easily obtained [14-15]. For measuring the interfacial activity, the method reported by Acevedo and coworkers [9] was used.

EXPERIMENTAL

All reagents were analytical grade and were used without further purification. The Cerro Negro crude oil used in this study came from the Morichal oil field (southeastern part of Venezuela) and has the following characteristics (wt %): $^{\circ}\text{API} = 8.1^{\circ}$, % C = 80.32, % H = 9.88, % S = 3.7, % Asphaltenes = 11.50, [V] = 367 ppm, [Ni] = 95.5 ppm, acidity = 3.7 mg KOH/g, Conradson Carbon = 17.22 %.

FTIR spectra were carried out using CH_2Cl_2 as solvent and KBr cells. CDCl_3 was used as solvent and TMS as reference for H- and ^{13}C -NMR analysis. VPO molecular weight determinations were carried out in CHCl_3 as solvent.

For the isolation of the total acid fraction (TAF), a column of quaternary alkylammonium chloride supported on a crosslinked styrene-divinylbenzene resin (Bio Rad AG-1, 200-400 mesh) was used as reported previously by Green and coworkers [14-16]. For the separation of the strong acid fraction (SAF) the method used was developed originally by McCarthy and Duthie [17].

The interfacial tension measurements were carried out using a toluene/water model system was used [9] (Robal Electronics Balance) and the values were reported at equilibrium at room temperature. The samples were dissolved in toluene and the concentrations were calculated with respect to the oleic phase. The pH of the aqueous phase was adjusted with KOH [9, 18].

RESULTS AND DISCUSSION

Total and strong acid fractions (TAF and SAF) were isolated from the crude oil by ion-exchange chromatography using a styrene-divinylbenzene resin [14-16] and KOH/SiO_2 [17] columns, respectively. In general, mass balances were between 90 and 95% with average percentages of extraction of 18% and 4% for TAF and SAT with respect to the original crude oil. The characterization by FTIR showed the presence of a band at 1710 cm^{-1} which was assigned to the carbonyl groups of the acid moiety [15-16]. Also, other bands were observed which corresponded very well with the reported values for: $\nu(\phi\text{-OH}) = 3590\text{ cm}^{-1}$, $\nu(\text{N-H})_{\text{arom}} = 3460\text{ cm}^{-1}$, $\nu(\text{C-H})_{\text{arom}} = 3000\text{ cm}^{-1}$, $\nu(\text{C-H})_{\text{aliph}} = 2800\text{ cm}^{-1}$, $\nu(\text{C}=\text{C})_{\text{arom}} = 1600\text{ cm}^{-1}$ [15-17]. From the analysis of the absorbance ratio of $\nu(\text{C}=\text{O})/\nu(\text{C}=\text{C})$ and $\nu(\phi\text{-OH})/\nu(\text{NH})$ bands and their total acid Numbers (Table 1) it can be concluded that SAF present higher concentration of carboxylic acid groups than TAF, whereas the later has more phenolic containing compounds than the former.

H-NMR characterization showed, besides the normal signals between 7.2 and 8.5 ppm for aromatic protons and between 0.1 and 3.8 ppm for aliphatic protons, a broad band in the range 9-10 ppm which was attributed to the carboxylic acid proton as reported in the literature [19]. ^{13}C -NMR analysis showed a small signal at 168 ppm which is consistent with the presence of carboxylic acid in TAF and SAF.

The interfacial activity vs pH was evaluated using a toluene/water model system and the results are shown in Fig. 1. As can be seen, this system presents very small interfacial activity in the pH range studied. On the other hand at pH greater than 13, a very small value for the interfacial tension ($<1\text{ dynes/cm}$) was obtained for the original Cerro Negro crude oil (CNC) as it is reported previously in the literature [7-9]. Furthermore, a reconstituted sample of the Cerro Negro Crude oil (prepared by mixing TAF and BNF in the 18/82 ratio) showed similar interfacial

activity than that found for the original CNC (Fig. 1). These results indicate that the separation method induced little changes on the interfacial properties on the crude oil as stated in the Introduction.

The effect of the pH on the interfacial activity of Cerro Negro crude oil and its fractions can be seen in Fig. 2A. It was found that the TAF present lower interfacial tension (2.1 dynes/cm) than those found for the original crude oil (5.3 dynes/cm) and BNT (4.6 dynes/cm) at 1000 mg/l and pH = 12. Similar results were obtained (Fig. 2B) by changing the concentration of the sample in the 100-15000 mg/l range at pH = 12. In general, the interfacial activity decreased in the order TAF > CNC > BNT.

In the same way, SAF showed lower interfacial tension (0.8 dynes/cm) than those determined for CNC (5.3 dynes/cm) and BNF (4.6 dynes/cm) at 1000 mg/l and pH = 12 (Fig. 3A). Also, a similar order of interfacial activity was found, SAF > CNC > BNT (Fig. 3B). From these results can be concluded that interfacially active compounds at high pH values are concentrated mainly in the acid fractions (TAF and SAF) of the crude as expected from the analysis of the literature [1-12].

Chemical characterization (FTIR, total acid number, H-NMR and molecular weight by VPO) and interfacial properties (interfacial tension at pH= 12, interfacial saturation, ISC, and excess, Γ , concentrations and area occupied at interphase) of Cerro Negro crude oil and its acid, basic and neutral fractions can be seen in Table 1. It is important to point out that in case of traditional surfactants, the ISC is better known as critical micellar concentration or CMC. Because the fractions studied in this work are very complex mixtures of a large variety of compounds and formation of micelles in these systems is not confirmed [20], it is preferred to use the term ISC instead of CMC. Therefore, ISC is defined as the concentration in which the interfacial tension remains constant at a given pH value.

As can be seen in Table 1, the interfacially active fractions TAF showed higher concentration of acids and phenols, measured by absorbance ratio of $\nu(\text{C}=\text{O})/\nu(\text{C}=\text{C})$ and $\nu(\phi\text{-OH})/\nu(\text{NH})$, in comparison with the crude oil and its basic and neutral fractions. It is reported that the intensity of these bands increases as the activity of the natural surfactants increases for stabilization of water/crude emulsion [10-12]. Also, it can be observed in Table 1 and Fig. 2 that interfacial activity increases (lower interfacial tension and ISC) as the acidity of the sample increases for TAF, CNC and BNT.

In the same way, H-NMR analysis showed that the percentage of aromatic protons in TAF is higher (7.5%) than those found for the CNC (5.9%) and BNT (5.1%) whereas the molecular weight of TAF is higher (929 g/mol) than CNC (638 g/mol). Therefore, it can be concluded that the hydrophobic portion of the natural surfactants has higher aromatic character and molecular weight whereas the hydrophilic region showed higher acidity and concentration of polar substituents in comparison with the original Cerro Negro crude oil.

As seen in Table 1, the strong acid fraction showed an interfacial tension value (measured above its ISC) similar to the original crude and TAF (0.7, 0.6 and 1.2 dynes/cm, respectively). However, the ISC found for SAF is approximately one fourth of CNC but two fold of TAF (1050, 4000, 650 mg/l, respectively). On the other hand, the molecular weight of SAF is higher (774 g/mol) than that found for CNC (638 g/mol) but smaller with respect to TAF (929 g/mol).

Also, the area occupied at the interface for SAT is greater (156 Å) than those found for CNC and TAF (113 and 132 Å, respectively). These results indicate that SAF has **lower interfacial activity per molecule** than TAF due to higher value of ISC, greater area occupied at interface but lower molecular weight of the former in comparison with the later extract. Therefore, the results can be explained in terms of a better hydrophilic-lipophilic balance of the TAF, (higher molecular weight, lower concentration of polar groups and higher total acid number) in comparison with the SAF. All the results presented in this work constitute an important contribution toward the understanding the chemical structure-surface activity relationships of the natural surfactants present in Venezuelan crude oil.

REFERENCES

- 1) Reisberg, J.; Doscher, T. M. *Producers Monthly*, **20**, 46 (1956).
- 2) Neuman, H. J. Erdon und Khole, **17**, 346 (1964).
- 3) Bartell, F. E.; Niederhauser, D. O., *Fundamental Research on Occurrence and Recovery of Petroleum*, American Petroleum Institute, N. Y., 57 (1946-7).
- 4) Schramm, L. L.; Smith, R. G.; Stone, J. A., *Aostr Journal of Research*, **1**, 5 (1984).
- 5) Moschopedis, S. E.; Speight, J. G., *Fuel*, **55**, 334 (1976).
- 6) Moschopedis, S. E.; Speight, J. G., *Fuel*, **55**, 187 (1976).

- 7) Seifert, W. K.; Howells, W. G., Amer. Chem. Soc., Div. Pet. Chem. Prepr., **14**, 73 (1969).
- 8) Seifert, W. K., Amer. Chem. Soc., Div. Pet. Chem. Prepr., **14**, 87 (1969).
- 9) Layrisse L.; Rivas, H.; Acevedo, S. J. Disp. Sci. Tech., **5**, 1 (1984).
- 10) Nordli, K. G.; Sjoblom, J.; Kizling, J.; Stenius, P. Colloids. & Surf., **57**, 83 (1991).
- 11) Sjoblom, J.; Mingyuan, L.; Christy, A. A.; Ronningsen, H. P., Coll. & Surf., **96**, 261 (1995).
- 12) Sjoblom, J.; Mingyuan, L.; Christy, A. A.; Gu, T. Colloids. & Surf., **66**, 55 (1992).
- 13) Urdahl, O.; Brekke, T.; Sjoblom, J., Fuel, **71**, 739 (1992).
- 14) Green, J. B.; Sturm, G. P., Jr.; Reynolds, J. W.; Thomson, J. S.; Yu, S. K.-T.; Grigsby, R. D.; Tang, S.-Y.; Shay, J. Y.; Hirsh, D. E.; Sanchez, V., U. S. Department of Energy, DE 90000200, Fossil Energy, Niper-161 (1988) and references therein.
- 15) Green, J. B.; Hoff, R. J.; Woodward, P. W.; Stevens, L. L., Fuel, **63** (1984).
- 16) Green, J. B.; Yu, S. K.-T.; Green, J. A.; Doughty, D. A.; Vogh, J. W.; Grigsby, R. D.; Vrana, R. P.; Thomson, J. S.; Carbognani, L., U. S. Department of Energy, DE 90000200, Fossil Energy, Niper-322 (1989).
- 17) McCarthy, R. D.; Suthie, A. H., J. Lipid Research, **3**, 117 (1962).
- 18) Acevedo, S.; Escobar, G.; Gutierrez, L.; Rivas, H.; Fuel, **71**, 619 (1992).
- 19) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C., Spectrometric Identification of Organic Compounds, Wiley, New York, p249 (1981).
- 20) Speight, J. G.; Wernick, D. L.; Gould, K. A.; Overfield, R. E; Rao, B. M., Savage, D. W. Revue de L'Institut Français du Pétrole, **40**, 51 (1985)

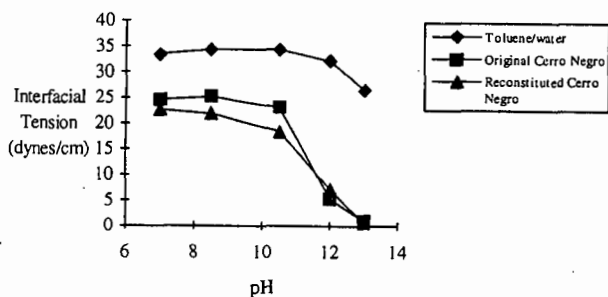


Fig. 1. Interfacial tension vs pH for original and reconstituted Cerro Negro crude oil. Concentration = 1000 mg/l. Toluene/water model system (pH = 12).

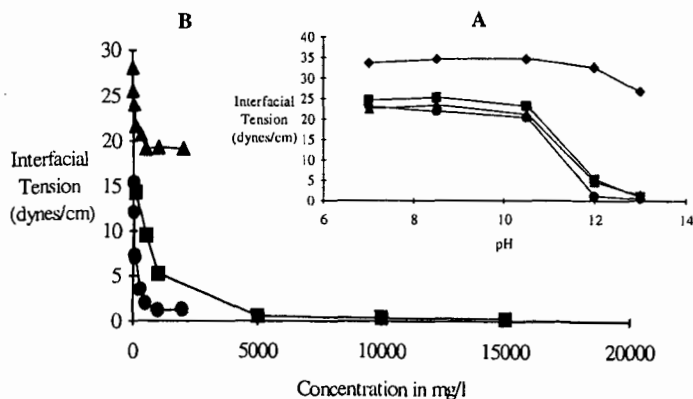


Fig. 2. Effects of (A) pH (at 1000 mg/l) and (B) concentration (at pH = 12) on the interfacial tension for Cerro Negro crude oil (CNC, ■) and its total acid (TAF, ●), basic and neutral (BNT, ▲) fractions using a toluene/water model system (♦).

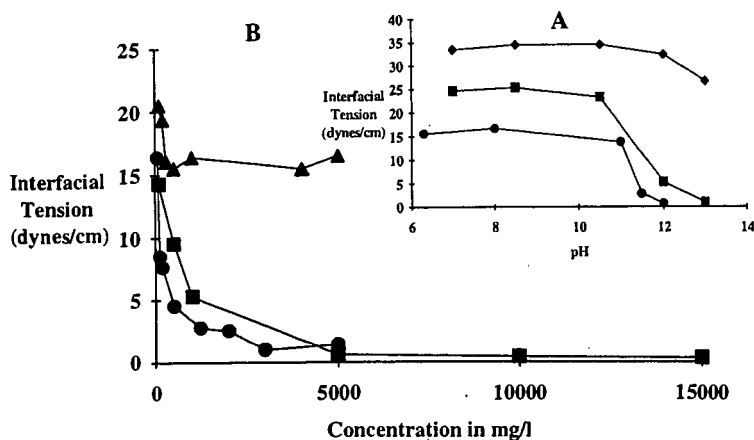


Fig. 3. Effects of (A) pH (at 1000 mg/l) and (B) concentration (at pH = 12) on the interfacial tension for Cerro Negro crude oil (CNC, ■) and its strong acid (SAF, ●), basic and neutral (BNF, ▲) fractions using a toluene/water model system (♦).

Table 1. Chemical and interfacial characterization of Cerro Negro crude oil and its acid, basic and neutral fractions^a.

| Chemical Characterization | Fraction | | | | |
|--|----------------------------|---------------------------|---------------------------|--------------------------|---------------------------|
| | CNC ^b (100%) | TAF ^c (18%) | BNT ^d (82%) | SAF ^e (4%) | BNF ^f (96%) |
| $\nu(\text{C=O})/\nu(\text{C=C})^g$ | 0.57 | 0.97 | 0.37 | 3.38 | 0.06 |
| $\nu(\phi\text{-OH})/\nu(\text{NH})^h$ | 0.18 | 0.64 | 0.50 | 0.52 | 0.77 |
| Total acid No. ⁱ | 3.7 | 4.1 | 0.95 | 71.8 | 0.2 |
| %H _{arom} ^j | 5.9 | 7.5 | 5.1 | 7.5 | 6.9 |
| %H _{alif} ^k | 93.9 | 92.5 | 95.0 | 92.9 | 93.1 |
| Mol. Weight. ^l | 638 | 929 | 477 | 774 | 518 |
| Interfacial Properties | | | | | |
| Interf. Tension. ^m | 0.6 | 1.2 | 11.1 | 0.7 | 15.5 |
| ISC ⁿ | 4000 | 650 | 500 | 1050 | 3700 |
| Interf. Area ^p | 113 | 132 | 187 | 156 | ° |
| Interf. Conc.ex. (Γ) ^q | 1.47 | 1.26 | 0.89 | 1.06 | ° |

^aThe fractions were separated by ion-exchanged chromatography according with the literature [14-17]. Numbers in bracket indicate percentage w/w with respect to Cerro Negro Crude oil. ^bCerro Negro Crude oil. ^cTotal acid fraction. ^dBasic and neutral fraction obtained from TAF separation. ^eStrong basic fraction. ^fBasic and neutral fraction obtained from SAF separation. ^gAbsorbance ratio between $\nu(\text{C=O})$ at 1700-1710 cm^{-1} and $\nu(\text{C=C})$ at 1600 cm^{-1} . ^hAbsorbance ratio between phenolic $\nu(\text{O-H})$ at 3590 cm^{-1} and aromatic $\nu(\text{N-H})$ at 3460 cm^{-1} . ⁱTotal acid number in mg of KOH/gr of sample. ^jPercentage of aromatic protons determined by H-NMR. ^kPercentage of aliphatic protons determined by H-NMR. ^lMolecular weight determined by VPO. Error $\pm 5\%$. ^mInterfacial tension (in dyne/cm ± 1) above its concentration of saturation for a toluene/water model system at room temperature and pH = 12. Interfacial tension without additive = 32.5 dyne/cm. ⁿIt did not show a typical Gibbs isotherm. ^pInterface saturation concentration in. mg/l. ^qArea occupied at the interface in \AA^2 . ^rInterfacial concentration in excess $\times 10^{10}$ moles/ cm^2 .